ON THE

Reaction of Ethyl and Methyl Alcohol

WITH

Paradiazometatoluenesulphonic Acid

IN THE

Presence of Certain Substances;

AND ON

Metatoluenesulphonic Acid.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

JOHN J. GRIFFIN.

1895.

EASTON, PA.:
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ON THE REACTION OF ETHYL AND METHYL ALCOHOLS WITH PARADIAZOMETATOLUENESULPHONIC ACID IN THE PRESENCE OF CERTAIN SUBSTANCES.

Introduction.

Since it became known that the statement of Griess to the effect that, when diazo compounds are boiled with alcohol the decomposition products are nitrogen, aldehyde, and a substance formed by the replacement of the diazo group by hydrogen, was not at all general; but that in some cases the ethoxy group, and not hydrogen, enters into the compound; various efforts have been made to determine the conditions that decide which of these two reactions, known as the alkoxy and hydrogen reactions respectively, will take place. Work was done in this laboratory on the influence of pressure and temperature on the reaction, and it was shown that increase of pressure and simplicity of the alcohol radical favor the alkoxy reaction.

Metcalf,[1] in studying the reaction of certain alcohols with paradiazometatoluenesulphonic acid, showed that when the diazo compound is decomposed in alcohol, both the alkoxy and hydrogen reactions take place, the former greatly predominating, though the ratio changes somewhat with varying conditions of temperature and pressure. A few years later Beeson,[2] in his investigations on the action of certain diazo compounds on methyl and ethyl alcohols, carried on in this laboratory, having discovered the fact that the presence of an excess of alkalies and of some other substances determined the hydrogen reaction, it was thought desirable to study similar reactions in the case of paradiazometatoluenesulphonic acid.

Preparation of Paradiazometatoluenesulphonic Acid.

As a starting point the paratoluidinemetasulphonic acid of

[1] Am. Chem. J., **15**, 301. [2] *Ibid*, **16**, 235.

commerce was taken. This was a light brown powder, slightly soluble in cold, readily soluble in boiling water. After boiling with animal charcoal, two, or at most three recrystallizations gave a pure white product, separating from the solution in prismatic needles. By adding a little hydrochloric acid with the animal charcoal to the boiling solution the first crystallization gave a nearly white product. 100 grams of the crude material yielded 85 grams of the pure acid.

Pechmann,[1] who obtained paratoluidinemetasulphonic acid by treating paratoluidine with fuming sulphuric acid, describes the product as of a sulphur yellow color which it was impossible to remove, and Metcalf,[2] who followed the same method of preparation, speaks of the difficulty of obtaining the acid in a pure white condition.

The pure white paradiazometatoluenesulphonic acid thus obtained was finely pulverized and diazotized by suspending it in alcohol of 92 per cent. and treating it with a strong current of nitrous fumes, produced by the action of nitric acid on arsenious oxide, in the manner described by Metcalf, and with substantially the same results.

100 grams of the acid were suspended in 30 cc. of alcohol, and the nitrous fumes passed through the emulsion for thirty minutes. The action was very slow at first, but soon increased as the mixture warmed up. The alcohol took on an orange color which deepened to a dark brownish red shade. The diazo compound was of a light pink tint, and settled readily to the bottom of the flask after shaking, while, on the other hand, the alcohol with the suspended acid would remain milky for some time. This rapid settling to the bottom was taken as indicative of the completion of the reaction. The diazo compound was filtered off by means of a filter-pump, washed with a small quantity of alcohol and some ether and then dried. The yield in this and subsequent experiments, approached closely to the theoretical amount, never falling below 95 per cent. Some of the diazo compound dissolved in the alcohol and, on standing, crystallized out. The compound when dry keeps for months in the dark, but exposed to the

[1] Ann. chem. (Liebig), **173**, 195. [2] Dissertation, 1890, and Am. Chem. J., **15**, 301.

light it slowly turns yellow. It is very stable, and small protions have been ground in a mortar without exploding.

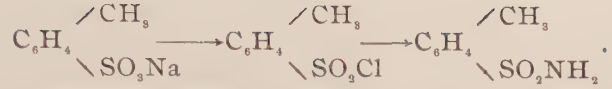
Decomposition of Paradiazometatoluenesulphonic Acid in Methyl Alcohol in Presence of Various Substances.

1. *In Presence of Sodium Methylate.*—In 80 cc. of pure methyl alcohol, redistilled over lime, 5 grams of metallic sodium were dissolved. The solution of sodium methylate was then placed in a beaker in a freezing-mixture, and when its temperature fell below zero, the paradiazometatoluenesulphonic acid was added, small portions at a time. There was immediate action, a gentle evolution of gas took place, the diazo compound gradually disappeared, and the alcohol took on a straw yellow color. After the addition of a few small portions, the temperature rose to 5° and the color deepened. No further addition of the diazo compound was made until the thermometer had again fallen below zero, and the temperature was kept below that point throughout the experiment. When about half the diazo compound had been added, an orange-yellow powder began to settle in the bottom of the beaker. The addition of the diazo compound was continued until 25 grams had been added; the beaker was then removed from the freezing-mixture and left to stand over night. During the decomposition, a slightly irritating odor, other than that of the alcohol, could be observed. When the reaction had ceased the material was poured into an evaporating-dish, and the methyl alcohol driven off by heating on a water-bath. The substance readily dried. When nearly dry, some volatile product, having a very irritating odor, and acting upon the eyes to produce an immediate flow of tears, began to be given off. The hard light-brown substance which remained in the dish was pulverized, and rubbed in a mortar, with its own weight (30 grams) of phosphorus pentachloride. The reaction was immediate and violent, and fumes of phosphorus oxychloride were given off. There remained behind a black viscid oil, together with a quantity of tarry products. This was poured into water, and a dark brown oil settled in the bottom of the vessel. Placed for some time in a test-tube,

in a freezing mixture, the oil did not solidify. This oil was washed with water several times and finally treated with strong ammonia, with which it readily reacted, going into solution and heating up considerably. Excess of ammonia was expelled by evaporating to dryness on a water-bath, and the residue extracted several times with ether. Upon distilling off the ether there remained behind a brown, syrupy liquid, which, on cooling, became solid and showed a crystalline structure. This was dissolved in boiling water and treated with animal charcoal and filtered. Upon cooling, small rhomboidal scales separated out, slightly brown in color. By several recrystallizations and treatment with animal charcoal, large clear white fern-shaped crystals were obtained which melted at 108°. This was the melting-point of the small quantity of metatoluenesulphonamide obtained by Metcalf from a mixture consisting for the greater part of paraethoxymetatoluenesulphonamide. The yield was 4.5 grams.

Another experiment was tried under similar conditions, with the exception of that of temperature, which was allowed to rise to 20°, and the results were essentially the same, with perhaps a slight increase in the tarry by-product. In this case, instead of pouring the mixture resulting from the decomposition of the diazo compound into an evaporating-dish, and driving off the alcohol, it was placed in an Erlenmeyer flask, and distilled off. There remained behind a light brown colored, porous mass, easily removed from the flask. This was heated on a water-bath till thoroughly dry. The same irritating odor was noticed. The alcohol which was distilled off was tested for aldehyde, and it responded at once to the silver mirror test. A solution of the light brown powder was also tested for aldehyde, and its presence was indicated in the same way. By treatment with phosphorus pentachloride and ammonia, as in the first case, four grams of the amide were obtained. In these and the subsequent experiments, no product other than the metatoluenesulphonamide was obtained. Its formation must, therefore have been through the following steps:

$$C_6H_3\begin{cases}CH_3\\SO_2H\,(m)\\NH_2\,(p)\end{cases} \longrightarrow C_6H_3\begin{cases}CH_3\\SO_3\,(m)\\N_2\,(p)\end{cases} \longrightarrow C_6H_4\begin{cases}CH_3\\ \\SO_3H\,(m)\end{cases} \longrightarrow$$



2. *In Presence of Sodium Carbonate.*—25 grams of the diazo acid were decomposed in 200 cc. of absolute methyl alcohol, in which 9 grams of dried sodium carbonate were suspended. When the alcohol had been cooled below zero, the addition of small portions of the diazo compound was begun. As the amount of substance added increased, the alcohol gradually took on a pink tinge, but, beyond an occasional bubble at long intervals, there was no apparent evolution of gas. The flask was then removed from the freezing-mixture, placed on a water-bath, and gently warmed to 30°, when a slow evolution of gas occurred. The flask was left standing over night. In the morning the alcohol was found to be colored brownish-red, and the sodium carbonate formed a layer at the bottom, seemingly in undiminished quantity. A thin layer of undecomposed or undissolved diazo compound covered the sodium carbonate. An occasional bubble of gas would rise through this upper layer. It was placed on a water-bath and heated to 35°, when the action became quite rapid, and continued till nearly all the sodium carbonate had disappeared. The temperature was then 46°. The flask was next connected with a condenser, and nearly all the alcohol was distilled off. The distillate gave a decided response to the test for aldehyde. The residual brown powder was very easily moved from the flask. Dried on the water-bath, it weighed 27 grams, and was darker in color than that obtained in the experiments with sodium methylate. 35 grams of phosphorus pentachloride were placed in a 500 cc. Erlenmeyer flask; the 27 grams of dark brown powder then added, and the flask connected with a condenser in order to obtain the volatile products of the reaction. The action began in less than a minute, and the contents of the flask became quite hot, though the action was not nearly as violent as in the experiment with sodium methylate. A great quantity of oxychloride fumes came over, but only a few drops of oxychloride were condensed in the receiver. The contents of the flask were poured into a large quantity of water, and a heavy, dark oil collected at the bottom of the ves-

sel. The oil, after thorough washing, was poured into a quantity of concentrated ammonia, and well shaken. After a few moments the contents of the flask heated up gently, and the oil disappeared, the ammonia turning a brown color. Left to stand over night, some brown, feathery crystals, together with some drops of dark, gummy substance, covered the bottom of the flask. The contents of the flask were placed in an evaporating-dish, and evaporated to dryness on a water-bath. The dry material was extracted several times with ether, the ether distilled off, and a brown, crystalline substance obtained. Boiled with water and animal charcoal, a yield of 12 grams of a light brown colored amide was obtained. A second experiment with sodium carbonate and methyl alcohol was performed, the alcohol being at the room temperature, 20°. A gentle evolution of gas began at once, and the temperature rose gradually while the diazo compound was added. It was not allowed to rise above 45°, being cooled when it reached that point by immersion in cold water. The remainder of the process was exactly as in the previous case, resulting in a like yield, 12 grams of amide.

3. *In Presence of Sodium Hydroxide.*—In this experiment, 7 grams of fused sodium hydroxide were broken up and placed in an Erlenmeyer flask with 200 cc. of methyl alcohol. Small portions of the diazo compound were added, and the action was immediate, the temperature, which was 21° at the beginning of the experiment, rising so rapidly that the flask was placed in ice-water and kept there throughout the experiment. After 25 grams of the diazo compound had been added, the flask was left standing till all action had ceased, when the alcohol was distilled off as in the preceding cases. On applying the silver mirror test to the alcohol which was distilled off, aldehyde was found to be present in it. After the alcohol had been evaporated off, and the residual gummy mass dried and powdered, it was treated with phosphorus pentachloride. The action was extremely rapid and violent. The thick black oil which resulted, was washed with water, and then treated with strong ammonia, resulting in a yield of 12 grams of amide.

4. *In Presence of Zinc Dust.*—In a flask containing 200 cc.

of absolute methyl alcohol, 10 grams of zinc dust were placed. The diazo compound was then added in small portions, the flask being well shaken after every addition. Action took place at once with a rapid rise of temperature from 17° at the beginning, to 30°. When this latter temperature was reached the flask was placed in ice-water. In this experiment the alcohol did not discolor for a long time, whereas in the other decompositions, a very small proportion of the whole quantity of the diazo compound sufficed to give the alcohol a decided red color. When 25 grams of diazo acid had been added, the alcohol was of a light straw color.

After all action had ceased, the solution was filtered to remove the residual zinc dust. The alcohol was then poured into a flask, connected with a condenser and distilled. A yellowish, syrupy liquid remained behind. This was poured into an evaporating-dish, and heated on a water-bath to dryness. During the drying, the irritating odors of the previous experiments were noticed. When dry, the substance was ground up in a mortar, and 32 grams of an almost white powder were obtained. Treated with phosphorus pentachloride, the action was very violent, great heat was developed, and but a small quantity of oil was obtained. This, however, was almost white, not like the dark viscid oil of the previous experiments. Treated with ammonia in the usual manner, 5 grams of pure white amide, melting at 108°, were obtained.

5. *In Presence of Calcium Carbonate.*—In this experiment 300 cc. of methyl alcohol and 15 grams of powdered calcium carbonate were taken. The diazo compound was added in small portions at a time, but no action was noticed. The flask was then placed on a water-bath, and heated up to 45°, but still there was no evolution of gas. The alcohol, however, became pink, probably from some of the diazo compound going into solution. 50 grams of the diazo acid were added, and the whole left to stand over night. In the morning the calcium carbonate covered the bottom of the flask, with the lighter, undissolved diazo compound forming a layer above.

From this experiment, it seems, therefore, that the presence of calcium carbonate has no influence whatever on the diazo decomposition; which entirely agrees with Beeson's[1] results

[1] Am. Chem. J., **16**, 235; and dissertation.

in his experiments with diazobenzene nitrate and calcite.

An excess, 17 grams, of zinc dust, was then added to the mixture. Bubbles of gas formed at once, and as the contents of the flask heated up, the reaction went on briskly. The alcohol, which was of a pink color, soon became colorless, and at the conclusion of the action, possessed the light yellow color observed in previous experiments with zinc dust. After filtering from the calcium carbonate and residual zinc dust, drying, and proceeding as before, a yield of 10 grams of pure white amide was obtained.

Decomposition of Paradiazometatoluenesulphonic Acid in Ethyl Alcohol in Presence of Various Substances.

1. *In Presence of Sodium Ethylate.*—3.5 grams of sodium were dissolved in 20 cc. of absolute ethyl alcohol, and the solution placed in a 500 cc. Erlenmeyer flask and cooled down to 5° below zero. The diazo compound was added in small portions at a time. Each portion sank at once to the bottom of the flask, but in a few moments rose rapidly to the surface, colored a dark red, and an evolution of gas began. The odor of aldehyde was very marked from the beginning. As the addition proceeded the solution thickened, and became very dark in color. The evolution of gas became sluggish and endured for a long time after all the diazo compound had been added. The temperature was kept below zero until 25 grams of the diazo compound had been added, when the flask was removed from the freezing-mixture, and the contents left to attain the room temperature.

The mixture was allowed to stand over night, then placed upon a water-bath, and the alcohol distilled off. A hard black mass remained in the flask. This could not be removed, and the alcohol was poured back into the flask and heated on the water-bath; but the mass remained hard. It was left standing two and a half days, but with no better result. The alcohol was distilled off again, and the mass dissolved readily in a small quantity of water. This solution was evaporated to dryness over a water-bath. The drying was a long and tedious process, the mass becoming gummy. This

same difficulty in drying the product which had been in contact with water, was noticed by Metcalf.[1] The dried mass was powdered and weighed 35 grams. It was of a dark brown color, much darker than the corresponding compound obtained from methyl alcohol. This was placed in a 500 cc. Erlenmeyer flask, which, after the addition of 45 grams of phosphorus pentachloride, was rapidly connected with a condenser, by means of rubber tubing, and shaken. The reaction took place very slowly, the flask heated up gradually, and a few drops of oxychloride distilled over. There remained a black viscous mass. This was shaken up with ether; the ether solution poured off, and the ether distilled off.

A thick black oil remained, and this was shaken up several times with water. Placed in a freezing-mixture for half an hour it did not solidify. The oil was then shaken up with ammonia, but the action was very feeble, and after the action some tar remained. The ammonia solution was poured off, evaporated to dryness, and the residue extracted several times with ether. 4 grams of dark-colored amide were obtained. The experiment was repeated with the same quantities of material, but no efforts were made to keep the temperature down. The only difference noted was in the rapidity of the reaction which, in the second experiment, was much greater than when the flask was kept in the freezing-mixture, but in neither case was it nearly as brisk as when methyl alcohol was employed. A yield of 3 grams of amide and a greater quantity of tarry matter than in the previous experiment, were obtained.

The alcohol which was distilled off in both these cases gave the mirror test for aldehyde.

2. *In Presence of Sodium Carbonate.*—9 grams of dried sodium carbonate were suspended in 200 cc. of absolute alcohol, and, after cooling the mixture to zero, 25 grams of the diazo compound were gradually added. There was no apparent action, beyond the alcohol becoming colored a pale yellow. Minute bubbles appeared after a few minutes. As the action seemed not to increase, the flask was taken from the

[1] Dissertation, page 8; and Am. Chem. J., **15**, 201.

freezing-mixture and placed on a water-bath. When its temperature was 32° the action became brisk, but not nearly as much as in the case of methyl alcohol and sodium carbonate. The odor of aldehyde was distinctly perceptible. The flask was kept on the water-bath till its contents attained a temperature of 50°. It was then removed, and left standing over night.

In the morning the alcohol was colored a deep red, and bubbles of gas were still rising to the surface. Upon heating the flask the evolution of gas became very rapid. When this had almost entirely ceased the alcohol was distilled off. The brown mass remaining behind was removed very easily and powdered. It weighed 35 grams. This was rubbed up in a mortar with an equal weight of phosphorus pentachloride. The action was gentle, and the product was shaken up with water, and then extracted with ether. 28 grams of a dark brown oil, which did not thicken in a freezing-mixture, were obtained. This was poured into 100 cc. of concentrated ammonia in an Erlenmeyer flask, and the flask and contents were shaken. The oil disappeared in a few minutes, the ammonia heated up and became brown in color. After evaporating to dryness, extracting with ether, and recrystallizing from water and animal charcoal, 10 grams of a pure white amide were obtained.

A second experiment was performed under similar conditions, with the exception that the oil obtained by the pentachloride treatment was not extracted with ether, but, after washing with water, poured into the concentrated ammonia.

The amide obtained after recrystallizing from water and animal charcoal weighed 8 grams, and was of a light brown color.

A third experiment was performed, the variation in this case consisting in using 90 per cent. alcohol in place of absolute alcohol. This experiment was performed at the room temperature. Upon the addition of the diazo compound there was a brisk evolution of gas but no odor of aldehyde. The contents of the flask heated up to above 40°. After standing a while it was heated on a water-bath to 45°, when the bubbles became larger, and the effervescence proceeded briskly for some

time, the sodium carbonate gradually disappearing till but a small portion of it remained. The odor of aldehyde was now perceptible. From this it seems that the reaction took place in two stages, the first being probably the formation of the sodium salt of paradiazometatoluenesulphonic acid, and the second the decomposition of this compound.

Proceeding as in the second experiment, 7 grams of a light brown amide were obtained.

3. *In Presence of Sodium Hydroxide.*—In this experiment an excess, 7 grams, of fused sodium hydroxide was broken up into small pieces and placed in an Erlenmeyer flask with 200 cc. of absolute ethyl alcohol. The experiment was begun at the room temperature. The reaction was similar to that with sodium ethylate, but the decomposition took place much more slowly than when ethyl alcohol and sodium hydroxide were used. After distilling off the alcohol, drying and powdering, 35 grams of a brown substance were obtained. Treating with phosphorus pentachloride, a black oil resulted. Upon washing this with water, quite a quantity of black tarry scum rose to the surface. The yield of amide obtained from this oil was 10 grams, and its color was brown.

4. *In Presence of Zinc Dust.*—In this experiment 300 cc. of absolute ethyl alcohol and 17 grams of zinc dust were taken. 50 grams of the diazo compound were slowly added. No freezing-mixture was employed, but the temperature was kept down by placing the flask in running water.

The evolution of gas was a little sluggish at first, but, as the contents of the flask heated up, it became brisk. The odor of aldehyde was noticed from the very beginning. When the reaction was over the alcohol remained limpid and of a light orange color, in distinction to the dark-red, syrupy liquid which resulted from the other experiment with ethyl alcohol. The alcohol was distilled off, leaving a hard, almost white residue on the bottom of the flask. This was removed by boiling with water, and the watery substance was then evaporated to dryness, which was readily done, and powdered, yielding 55 grams. Treated with phosphorus pentachloride, the action was very violent, and a small quantity of a brown oil was obtained. This, after washing with water, gave 7 grams of a nearly pure white amide.

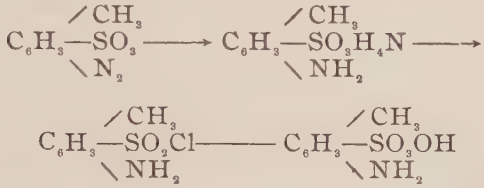
5. *In Presence of Ammonia.*—200 cc. of absolute methyl alcohol were saturated with dry ammonia gas and the solution was cooled to zero. Upon the addition of the diazo compound there was no apparent action. After waiting some time the flask was removed from the freezing-mixture and its contents were allowed to take the room temperature (20°), when action began at once. As more diazo compound was added the temperature rose rapidly, and the flask was cooled by placing it in a dish of cold water. Upon the completion of the reaction the alcohol was distilled off, the residue removed from the flask, dried, and powdered. The powder was treated in a mortar with an equal amount of phosphorus pentachloride; the reaction was very violent; fumes of phosphorus oxychloride were given off, but in place of the appearance of an oil the mixture in the mortar thickened and became solid. Water was added to this, upon which the mass foamed up, and after the reaction was over bunches of yellow needles appeared throughout the dark red liquid.

A quantity of crystals was removed and washed with water. They were found to be very soluble in water. Repeated boiling with animal charcoal failed to remove or lessen their yellow color. Heated up to 300°, they charred without melting. On adding strong hydrochloric acid to a solution of the substance, white needles, similar in appearance to the original paratoluidinemetasulphonic acid crystallized out. It was supposed that it might be the ammonium salt of paratoluidinemetasulphonic acid, and to test this about 20 grams of it was diazotized in the usual manner, and the diazo compound, similar in appearance to that obtained heretofore, was then decomposed in absolute methyl alcohol, to which an excess of fused sodium hydroxide had been added. The decomposition took place in all respects similar to that of the diazo acid in methyl alcohol and sodium hydroxide. On drying, powdering, and treating with phosphorus pentachloride, a dark-colored oil was obtained, which was washed and treated with ammonia. The resulting amide was extracted with ether, boiled with water and animal charcoal, and brown crystals were obtained which, by repeated purifications, gave large pure white scales, of exactly the same appearance as

the recrystallized amides previously obtained, and melting at the same temperature.

The experiment was repeated, using ethyl alcohol, with like results.

Hence the decomposition of paradiazometatoluenesulphonic acid in ammoniacal alcohol, must have taken place as follows:



A comparison of the different yields of purified amides was made as follows, the numbers representing the yield in grams of pure amide obtained from the decomposition of 100 grams of the paradiazometatoluenesulphonic acid.

	In methyl alcohol.	In ethyl alcohol.
With sodium.....	24.8	19.0
" sodium carbonate ..	36.0	33.0
" sodium hydroxide..	33.0	24.0
" zinc dust.....	17.0	24.0

Each weight is the average of at least three experiments.

From these experiments it is seen that the sodium carbonate reaction yielded the largest amount of amide. The compound resulting from the decomposition ol the diazo acid in presence of sodium carbonate, and which contained the excess of sodium carbonate originally added, was also the one most slowly acted upon by phosphorus pentachloride.

On the other hand, with the exception of the zinc dust reaction, all the others gave a quantity of tarry matter upon treatment with phosphorus pentchloride.

The apparent purity of the oil obtained by treating with phosphorus pentachloride the product of the decomposition of paradiazometatoluenesulphonic acid in the presence of zinc dust; the absence of all traces of tarry matter, and the large clear white crystals of amide which the very first crystallization yielded, marked the zinc reaction as by far the cleanest method of decomposition. The great disparity in the yields

of amide obtained by this and the other methods of decomposition, was not, however, in its favor.

It was thought that the heat of the reaction might have decomposed or volatilized a part of the sulphonchloride formed, and experiments were made with a less violent chlorinating agent than phosphorus pentachloride. Accordingly 50 grams of the diazo compound were decomposed in 300 cc. of methyl alcohol and 17 grams of zinc dust. After the decomposition, the solution was filtered and evaporated to dryness, 55 grams of a light-brown powder being obtained. This was added in small portions at a time, to 70 grams of phosphorus trichloride, contained in a 300 cc. round-bottomed flask. After a few grams had been added small bubbles began to appear, coming from the powder, which darkened somewhat in color, and became gummy. As the addition of substance went on, the temperature rose very slightly. After the whole had been added the flask was put aside over night.

In the morning the contents of the flask consisted of a brown gum, which covered the bottom, and an almost clear liquid on top. Most of the clear liquid, the greater part of which was phosphorus trichloride, was poured off, placed in a flask, and distilled under diminished pressure. There remained behind a small quantity of a slightly yellow oil. This was shaken up with water; it became lighter in color, diminished somewhat in quantity, and settled readily to the bottom of the flask.

The flask containing the gummy substance and the remainder of the clear liquid, was then connected with a condenser, and heated upon a water-bath under diminished pressure. Some more phosphorus trichloride came over. When distillation had ceased the flask was removed, and the slightly yellow liquid above the gummy material poured into water. It settled at once to the bottom. Water was added to the flask containing the brown gum, and this dissolved slowly, giving off small globules of oil which gathered together at the bottom. The three portions of oil were put together and washed repeatedly with water.

The amide was made by pouring the oil into a 500 cc. Erlenmeyer flask containing from 150 to 200 cc. of strong ammo-

nia, and shaking vigorously. In a few minutes the contents of the flask became warm and the oil dissolved, forming a clear, light-yellow solution. Upon cooling, large slightly yellow crystals of the amide separated out. After filtering, the mother-liquid was evaporated to dryness and the residue extracted with ether, which resulted in a still smaller addition to the total amount of amide obtained. After boiling with animal charcoal, the first crystallization yielded, from 100 grams of the diazo compound, 45 grams of large pure white fern-shaped crystals, which melted sharply at 108°.

The decomposition was repeated, using absolute ethyl alcohol in place of methyl alcohol. The decomposition did not take place as readily as when methyl alcohol was employed, but, upon slightly warming the alcohol, it became rapid. The alcohol remained nearly colorless throughout the experiment, while when methyl alcohol was used, it turned to an orange color. The yield of amide was a little greater than by the methyl alcohol method; 100 grams of the diazo acid giving 50 grams of pure amide.

The results obtained by heating the product of the diazo decomposition in presence of zinc dust with phosphorus trichloride, suggested a like experiment with that obtained by decomposing the diazo acid in presence of sodium carbonate.

Because the amides obtained by treating the residue, after the decomposition in presence of sodium carbonate, with phosphorus pentachloride and ammonia respectively approached that from the zinc dust reaction in whiteness and surpassed it in quantity, it was thought the substitution of the trichloride for the pentachloride of phosphorus, would lead to a larger and cleaner yield of metatoluenesulphonchloride.

Accordingly, about 25 grams of the diazo compound were decomposed in absolute ethyl alcohol in which 8 grams of dried sodium carbonate were suspended.

The reaction took place as in the like experiments previously performed, and about 30 grams of dried material were obtained. This was powdered, and added little by little, to 30 grams of phosphorus trichloride contained in a round-bottomed flask. Each small portion added settled to the bottom, and there was no appearance of any change taking place. When

the whole amount was added, the powder absorbed the liquid trichloride, but the contents of the flask did not warm up, nor was any other indication of a reaction noticed. Left to stand over night, its appearance was unchanged in the morning.

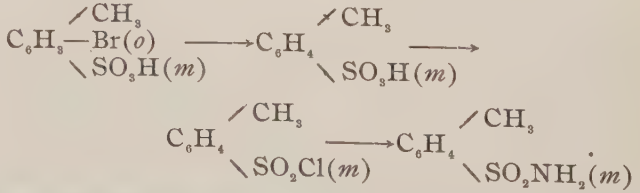
The flask was next connected with a reflux-condenser, and heated on a water-bath for two hours. A portion of the moist powder was then removed from the flask and thrown into cold water. There was the usual reaction between phosphorus trichloride and water, but no trace of an oily sulphonchloride. The substance was therefore removed from the flask and rubbed in a mortar with 30 grams of phosphorus pentachloride, resulting in the usual quantity of liquid metatoluenesulphonchloride, which was converted into the amide.

From this experiment it was concluded that the product obtained when the diazo compound was decomposed in presence of sodium carbonate would not react with phosphorus trichloride and all subsequent yields of sulphonchloride were obtained by the zinc dust and phosphorus trichloride treatment.

Metatoluenesulphonamide.

Having on hand a quantity of pure amide, obtained as a result of the preceding experiments, its properties were carefully studied and compared with the metatoluenesulphonamides described in the literature.

The amide was first mentioned, in 1873, by Müller,[1] who made it by reducing the barium salt of orthobrommetatoluenesulphonic acid, by means of sodium amalgam; and then by the phosphorus pentachloride reaction forming the sulphonchloride, which, treated with ammonia, gave the amide. The transition from the orthobrommetatoluenesulphonic acid to the amide, he supposed took place as follows:

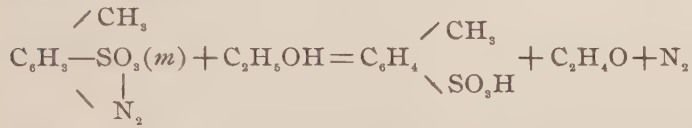


Müller describes the amide as easily soluble in ether, alco-

[1] Ann. chem. (Liebig) **169**, 51.

hol and ammonia, and as crystallizing from water at 40° in large scales, and from water at 20° in slender needles. Its melting-point was 90°–91°.

A year later Pechmann[1] obtained what he claimed to be metatoluenesulphonamide by decomposing paradiazometatoluenesulphonic acid in alcohol under pressure, according to the following equation:



From this acid he obtained an amide, like Müller's, soluble in hot water, alcohol, and ether, but which crystallized in rhombic scales and in brilliant leaves and needles, and melted "somewhere below 100°."

The amide was next obtained in 1875, by Pagel,[2] who also employed the diazo reaction, making first the diazo compound of orthotoluenesulphonic acid, changing this into the bromtoluenesulphonic acid, removing the bromine by long-continued treatment with sodium amalgam, and then proceeding to the amide by the usual reactions. Pagel's amide was tolerably easily soluble in cold water, much more so in hot water, and easily soluble in alcohol, chloroform, and ether. From all these solvents it crystallized out in large leaves, which melted at 104°.

In 1877, Beckurts[3] described an amide which he obtained by fractional crystallization from a mixture of amides. But this product, and that obtained two years later by Claesson and Wallin,[4] was a mixture of the para and ortho compounds, as will be shown in the second part of this thesis.

In 1879, F. H. S. Muller,[5] by treating the metadiazotoluene salts with sulphurous acid, obtained an amide melting at 107°. This also was probably impure, for an anilide obtained from the same sulphonchloride, had a much lower melting-point than the one which will be described further on.

1 Ann. chem. (Liebig), **173**, 195.
2 Ann. chem. (Liebig), **176**, 297.
3 Ber. d. chem. Ges., **10**, 943.
4 *Ibid*, **12**, 1848.
5 Ber. d. chem. Ges., **12**, 1348.

Neville and Winther,[1] (1880), by heating orthodiazotoluenesulphonic acid under pressure with alcohol, and by reduction of bromotoluenesulphonic acid by means of sodium amalgam, obtained a toluenesulphonic acid, which gave, on treating its potassium salt with phosphorus pentachloride, a sulphonchloride, and an amide which melted at 106.5°–107.5°.

Chase Palmer,[2] in 1882, repeated Hubner and Müller's process of obtaining the amide, and found a product identical in all its properties with that described by these investigators.

In 1886, Klason[3] prepared the amide after the method of Pechmann, and found it to have a melting-point of 108°, crytallizing in monoclinic scales and octahedra.

In the same year Vallin,[4] admitting the evidence of the impurity of the amide obtained by himself and Klason,[5] made the compound by the method of Pechmann and described it as crystallizing from water in leaves melting at 107°, and from alcohol in monoclinic crystals which melted at 108°. About this time, also, Noyes and Walker[6] made what they claimed to be the metatoluenesulphonamide by treating orthobromtoluene with fuming sulphuric acid, making the sodium salt and eliminating the bromine atom by means of zinc dust. The sodium salt was then treated with phosphorus pentachloride and the oily chloride thus obtained converted into an amide which melted at 90°–91°.

The next contribution to our knowledge of metatoluenesulphonamide was made by Metcalf,[7] in his work "On the Reaction of Certain Alcohols with Paradiazometatoluenesulphonic Acid," which showed that when this acid is decomposed by boiling with alcohol, both the alkoxy and the hydrogen reactions take place, the former to a much greater degree than the latter. Metcalf succeeded in separating a small quantity of the metatoluenesulphonamide from mixtures of it and paraethoxymetatoluenesulphonamide. He found

[1] J. Chem. Soc., **37**, 628.
[2] Am. Chem. J., **4**, 140.
[3] Ber. d. chem. Ges., **19**, 2887.
[4] Ber. d. chem. Ges., **19**, 2952.
[5] *Ibid*, **12**, 1848. The names of these two investigators were written Clæsson and Wallin.
[6] Am. Chem. J., **8**, 186.
[7] Dissertation, 1890, and Am. Chem. J., **15**, 301.

for these specimens melting-points ranging between 95° and 108°.

The amide which was obtained in the experiments herein described was carefully compared with that described by the above-mentioned investigators.

The specimens resulting from the phosphorus pentachloride reaction were boiled with animal charcoal and recrystallized six times. That which resulted from the sulphonchloride obtained by the phosphorus trichloride treatment, gave pure white crystals after its first recrystallization. From concentrated solutions the amide came down in brilliant hexagonal scales, and from more dilute solutions it separated out in beautiful large fern-like growths. It was soluble to a very slight extent in cold water, but easily soluble in hot water at a temperature of 70°. It was exceedingly soluble in alcohol, from which it crystallized in large monoclinic prisms.

Analyses of the amide gave the following results:

I. 0.3020 gram of the amide gave 0.5445 gram of carbon dioxide.

II. 0.3003 gram of the amide gave 0.5425 gram of carbon dioxide.

III. 0.3020 gram of the amide gave 0.1472 gram of water.

IV. 0.3003 gram of the amide gave 0.1450 gram of water.

V. 0.2391 gram of the amide gave 0.3302 gram of barium sulphate.

VI. 0.2910 gram of the amide gave 0.3950 gram of barium sulphate.

VII. 0.2210 gram of the amide gave 0.0202 gram of nitrogen.

VIII. 0.1800 gram of the amide gave 0.0149 gram of nitrogen.

IX. 0.2185 gram of the amide gave 0.0178 gram of nitrogen.

The sulphur determinations were made by Liebig's method. Nitrogen determination VII was made by the Dumas method; VIII and IX were made by Wilfarth's modification of the Kjeldahl method, and were made by Mr. J. W. Lawson, of this laboratory, who also made the carbon and hydrogen determinations.

	Calculated for $C_6H_4<^{CH_3}_{SO_2NH_2}$.	Found. I.	II.
C	49.12	49.17	49.26
H	5.26	5.40	5.36
S	18.71	18.92	18.73
N	8.18	8.15	8.28–8.15

The amide obtained by Müller[1] was described as crystallizing at 20° in slender needles. Though a great many observations were made, in no case did the amide come down in this form, hexagonal scales sometimes bunched in fern-shaped leaves, being the rule without exception.

Pechmann's amide came down in rhombic scales and needles, and though it melted at 104°, was far from being pure metatoluenesulphonamide, for, as evidenced by Metcalf's work, it contained a large quantity of paraethoxymetatoluenesulphonamide. Pagel's amide differed from that herein described in being tolerably easily soluble in cold water and in crystallizing from all its solvents in large leaves. The other amides referred to above, which were prepared after the methods of Müller and Pechmann, or a combination of both, cannot be considered as pure products.

Decomposition of Metatoluenesulphonamide.—As a test of the purity of the amide obtained from the product of the diazo decomposition in presence of alkalies and other substances, the experiment by which Otto[2] showed that Beckurt's amide was a mixture of the para and ortho componnds was performed.

15 grams of the amide were heated to 150° with concentrated hydrochloric acid, in a sealed tube, for four hours. The product of the reaction was very easily soluble in cold water, and the solution was repeatedly boiled down with water till free of hydrochloric acid. It was then treated with potassium hydroxide solution until all the ammonia was driven off. The potassium salt thus formed was very easily soluble in hot 95 per cent. alcohol, from which it crystallized out on cooling in a mass of fine needles. These crystals were dried in an air-bath at a temperature of 140°, powdered, and treated with an equal weight of phosphorus pentachloride. The reaction was

[1] Ann. Chem. (Liebig), **169**, 51.

[2] Ber. d. chem. Ges., **13**, 1292.

quiet and gentle, and a quantity of colorless oil was the result. Poured into cold water, a white scum covered the surface of the oil, but this disappeared on standing. The oil was separated from the water, poured into a test-tube and placed in a freezing-mixture for half an hour. At the expiration of this period it seemed to be as limpid as in the beginning, and showed no trace of a solid formation.

Oxidation of Metatoluenesulphonamide.

Another experiment was made, having for its aim the oxidation of metatoluenesulphonamide to metasulphaminebenzoic acid. To a mixture of 80 grams of concentrated sulphuric acid diluted with three times its volume of water, and 60 grams of potassium bichromate, 20 grams of metatoluenesulphonamide were added. The flask containing the mixture was connected with a reflux-condenser and heated gently over a low flame. The action began almost immediately, and became so energetic that cold water had to be added to the contents to prevent foaming over. After boiling for an hour, the oily layer of melted amide which covered the surface entirely disappeared, and the flask was removed and its contents, after cooling, were poured into cold water. A mass of crystals separated out. These were drained by means of a filter-pump, and washed with water till free from all bichromate color. They were then treated on the funnel with cold sodium carbonate solution, when most of the acid dissolved. The substance which remained on the filter was examined and proved to be pure metatoluenesulphonamide. It weighed about 2 grams.

Metasulphaminebenzoic Acid.

The sodium salt, which passed in solution through the filter, was treated with hydrochloric acid and a quantity of minute scales separated out. These were filtered off, dried, and recrystallized. They gave a melting-point of 233° (uncorrected). From the 20 grams of metatoluenesulphonamide a yield of 12 grams of the metasulphaminebenzoic acid resulted. It was carefully compared with the metasulphaminebenzoic acid which Limpricht and Uslar[1] obtained by heating together

[1] Ann. chem. (Liebig), **106**, 36.

sulphobenzamide and potassium hydroxide, and which was described as separated from cooled mixture in scales which melted above 200°. This acid was further described as sparingly soluble in cold water, more easily in ether, and very soluble in alcohol. Kept in a molten state for ten minutes, it stiffened on cooling to a crystalline mass easily soluble in water. Its barium salt was made by adding barium carbonate to a boiling solution of the acid. This was easily soluble in water, from which it crystallized out in small masses possessing a "wavellite"[1] structure, and containing four molecules of water of crystallization. Its silver salt consisted of long silky needles which contained two molecules of water of crystallization and did not blacken on boiling or long exposure to the light.

A small portion of the metasulphaminebenzoic acid made by oxidizing metatoluenesulphonamide, was gently heated upon platinum foil. It behaved similarly to Limpricht and Uslar's acid, volatilizing and passing off in white fumes free from the irritating effect of the fumes of benzoic acid. About one gram of the acid was heated in a test-tube in a sulphuric-acid bath to 245°–250° for forty-five minutes. Upon cooling, it stiffened to a brown, glassy mass, which was easily soluble in cold water, from which it crystallized out, on evaporating down the solution, in long needles.

Barium Salt of Metasulphaminebenzoic Acid.—The barium salt of the acid was made by neutralizing a boiling solution of the acid by means of pure barium carbonate. The undecomposed carbonate was filtered off and the solution evaporated down. Upon standing, small radiating nodules formed, which corresponded to the "wavellite" character of Limpricht and Uslar's barium salt.

The analysis of the barium salt showed its composition to be $\left(C_6H_4\begin{smallmatrix}CO_2\\SO_2NH_2\end{smallmatrix}\right)_2Ba+4\frac{1}{2}H_2O$.

I. 0.2345 gram of the barium salt, dried by exposure to the air, lost, upon being heated to 180°, 0.0306 gram water.

II. 0.3022 gram of the salt, gave off at 180°, 0.0394 gram water.

[1] "Wawellitartigen."

III. 0.2039 gram of the anhydrous barium salt, gave upon ignition with sulphuric acid, 0.0880 gram of barium sulphate.

IV. 0.2623 gram of the anhydrous salt, gave 0.1126 gram of barium sulphate.

	Calculated.	Found. I.	II.
H_2O	13.10	13.05	13.03
Ba	25.51	25.37	25.24

The dehydrated salt takes up water very rapidly, which makes its weighing difficult. The difference in results for the water of crystallization of this and Limpricht's and Uslar's determination may be due to this, and also to the fact that their barium salt was dried over sulphuric acid, and was heated but to 110°.

Silver Salt.—The silver salt was made by boiling a solution of the acid with silver carbonate. It was soluble to a slight extent in boiling, and insoluble in cold water. From hot water it crystallized out in long, fine needles, which slowly blackened upon exposure to the light. It contained no water of crystallization, and analysis showed that it corresponded to the formula $C_6H_4\begin{cases}COOAg\\SO_2NH_2\end{cases}$.

I. 0.2256 gram of the salt gave 0.0779 gram silver.

II. 0.2710 gram of the salt gave 0.0945 gram silver.

	Calculated.	Found. I.	II.
Ag	35.06	35.53	34.90

Limpricht and Uslar ascribed two molecules of water of crystallization to this salt.

On the whole, if we except the water of crystallization of the silver salt, there are enough points of similarity between the salts of metasulphaminebenzoic acid obtained by the oxidation of metatoluenesulphonamide, and those of Limpricht and Uslar's compound, to indicate the identity of both substances.

ON METATOLUENESULPHONIC ACID.

Introduction.

The action of sulphuric acid on toluene was first investigated by Jaworsky,[1] who described one toluene-sulphonic acid as the resulting compound.

In 1869, Engelhardt and Latschinoff[2] heated toluene with sulphuric acid, and made the potassium salt of the resulting acid. This crystallized out in two forms; prisms which were difficultly soluble, and needles which were more easily soluble in water. These two potassium salts were fused with caustic potash and gave two isomeric cresols, the para and ortho compounds.

Barth,[3] working in a similar manner, obtained by fusing the crude mixture of potassium salts, para-oxybenzoic and salicylic acids.

Anna Wolkow[4] confirmed this work, but ascribed the meta position to the sulphon group in the acid which passed over into salicylic acid, and further, made two sulphonchlorides, one liquid and one solid, and two amides, that from the α or para acid melting at 137°, and that from the β or, as it was then called, the meta acid melting at 153°–154°.[5]

Fittig and Ramsay,[6] in order to settle definitely the position of the sulphon group in the acid which Anna Wolkow called the metatoluenesulphonic acid, proceeded as follows: They treated toluene with sulphuric acid, made the isomeric potassium salts, and separated as far as possible by fractional crystallization, the para salt. The mother liquid, which contained some of the para and an isomeric salt which was either ortho or meta, was then evaporated to dryness and thoroughly mixed with potassium cyanide. This mixture was distilled in an iron retort; the oily liquid which came over was heated with caustic potash till free from ammonia. After washing with ether, the potassium salt was acidified and the toluic acid

[1] Ztschr. Chem. **1**, 272.
[2] *Ibid*, (1869) 617.
[3] Ann. chem. (Liebig), **152**, 91.
[4] Ztschr. Chem. (1870) 321.
[5] This was previous to V. Meyer's work on the orientation of the hydroxybenzoic acids.
[6] Ann. chem. (Liebig), **168**, 242.

extracted with ether. This was a mixture of paratoluic with either ortho- or metatoluic acid. An easy method of separation was found by treating the calcium salts with alcohol, in which the para salt was not soluble. By this means they obtained, not the meta, but the orthotoluic acid. They further confirmed their work by oxidizing this orthotoluic acid by means of a mixture of potassium bichromate and dilute sulphuric acid, and obtained as a product neither isophthalic nor terephthalic acid, which showed conclusively that the isomeric acid formed together with paratoluenesulphonic acid, when toluene is treated with sulphuric acid is not the meta, but the para compound.

The next contribution to our knowledge of the isomeric toluenesulphonic acids, was a consequence of Hübner and Post's[1] work on bromotoluene and the behavior of its hydrogen atoms.

By the action of sulphuric acid on crystallized bromotoluene, which they showed to be a para compound, two isomeric bromotoluenesulphonic acids were obtained, which they designated as the α and β parabromotoluenesulphonic acids. The β acid was treated with sodium amalgam in order to remove the bromine atom, and the toluenesulphonic acid thus obtained, was fused with potassium hydroxide. Salicylic acid was obtained, which was evidence that the sulphon group was in the position ortho to the methyl group. It was, therefore, by exclusion, concluded that the α acid must have the sulphon group in the meta position.

F. C. G. Müller[2] made the barium salt of orthobromtoluenesulphonic acid and treated it, in solution, with sodium amalgam, in order to remove the bromine atom from its molecule. The excess of alkali was neutralized with sulphuric acid, the sodium sulphate removed by evaporation and crystallization, and the residue dried. The dried mass was treated with phosphorus pentachloride, and an oily toluenesulphonchloride was obtained. This was heated with water to 130°, and the resulting acid mixture was freed from hydrochloric acid by evaporation and the passage of a current of air through it. The toluenesulphonic acid was obtained as a syrup, which stiffened to a crystalline condition. Various salts of the acid

[1] Ann. chem. (Leibig), 169, 47. [2] Ann. chem. (Liebig) 169, 47.

were made, some of which will be described later on. The amide obtained melted at 90°–91°. Because this toluenesulphonic acid differed from both the ortho and para acids, Müller considered it to be metatoluenesulphonic acid.

About the same time, F. Gervor[1] made orthodiazotoluenesulphonic acid by subjecting orthotoluidinesulphonic acid to the action of nitrous fumes. The diazo compound was decomposed in alcohol under pressure. The sodium salt of the sulphonic acid obtained was made, and gave upon treatment with phosphorus pentachloride, a fluid sulphonchloride, which was converted by the action of ammonia into an amide melting at 148°, and differing in this and other properties, from the ortho and para amides previously known.

In 1874 Pechmann[2] obtained a quantity of paratoluidinemetasulphonic acid by heating sulphuric acid with paratoluidine, and crystallizing out the paratoluldineorthosulphonic and the disulphonic acids formed, leaving the paratoluidinemetasulphonic acid, on account of its greater solubility, in solution.

From this solution the paratoluidinemetasulphonic acid crystallized out in sulphur-yellow needles which could not be decolorized by repeated boiling with animal charcoal. By precipitation from its salts, however, it was obtained colorless. It was difficultly soluble in cold water, one part of acid requiring ten parts of water for its solution.

The diazo compound was made by suspending the finely divided acid in alcohol, and treating it with nitrous fumes. This was then decomposed by heating it under pressure with alcohol.

Various salts of the resulting sulphonic acid were made which showed some differences from those of Müller, also an amide which melted somewhat below 100°.

In 1875, Pagel,[3] working on orthotoluidinesulphonic acid, obtained a toluenesulphonic acid which resembled Müller's meta acid.

A mixture of alcohol and sulphuric acid was neutralized with lime, and the resulting calcium ethyl sulphate wasdecom-

[1] Ann. chem. (Liebig), **169**, 383. [2] *Ibid*, **173**, 195.
[3] Ann. chem. (Liebig) **176**, 297.

posed by the addition of a solution of the orthotoluidine salt of oxalic acid. By filtration and crystallization, crystals of orthotoluidine ethyl sulphate were obtained, which were decomposed into alcohol and orthotoluidinesulphonic acid by being heated to 180°–200° in an air-bath.

The orthotoluidinesulphonic acid was changed into the diazo compound, and this transformed into bromotoluenesulphonic acid.

By proceeding as Müller did, a toluenesulphonic acid was obtained which agreed tolerably well with Müller's metatoluenesulphonic acid, if we except the melting-point of the amide, which Pagel found to be 104°.

In 1877, H. Beckurts,[1] seeking for a method by which to obtain a good yield of pure orthotoluenesulphonic acid heated a mixture of ordinary sulphuric acid and toluene and made the potassium salts of the resulting sulphonic acids in the usual manner. By treatment with phosphorus pentachloride a mixture of sulphonchlorides was obtained, from which the paratoluenesulphonchloride crystallized out upon cooling the mixture to 15° below zero.

The remaining liquid sulphonchloride was transformed into the amide compound, which was purified and subjected to fractional crystallization. Two compounds were obtained, one difficultly soluble in alcohol, which melted at 153°–154°, the other easily soluble in the same medium, and melting at 104°. From this work, Beckurts concluded that the action of sulphuric acid on toluene, resulted in the formation of the three isomeric sulphonic acids. The work was pursued further, and some of the amide heated with hydrochloric acid in a sealed tube to 150°. The ammonium salt of the acid was thus obtained, and from a portion of this, treated with barium hydroxide, the barium salt. From a comparison of these salts with the ammonium and barium salts obtained by Müller, Beckurts asserted that they were salts of metatoluenesulphonic acid.

Fahlberg,[2] working in this laboratory, doubted the statement that Beckurts had obtained metatoluenesulphonic acid, because, though his product showed differences from the ortho and para

1 Ber. d. chem Ges., **10**, 943.
2 Am. Chem. J. **1**, 170; Ber. d. chem. Ges. **10**, 1048.

compounds, he neglected to prove its constitution by converting it into an oxybenzoic acid. Fahlberg repeated Beckurts' work, with the sole exception that water, and not alcohol was used as the medium for fractional crystallization.

The liquid sulphonchloride, from which no more solid parasulphonchloride separated out when cooled to 15° below zero, was treated with aqueous ammonia. As products there were obtained α-toluenedisulphonamide, melting at 186°–187°, and a yellow mixture of amides. This latter he subjected to fractional solution; whereby only a portion dissolved. The undissolved amide melted at 153°–154°, and gave upon fusing with caustic potash, salicylic acid. Therefore it was orthotoluenesulphonamide. From the soluble portion of the mixture, two compounds were obtained by fractional crystallization. That less soluble, on purification, proved also to be orthotoluenesulphonamide.

From the solution of the more soluble portion an amide crystallized out, which melted at 120°, but repeated purifications with animal charcoal lowered the melting-point to 108°, where it remained constant. A quantity of the amide which melted at 108° was oxidized by means of potassium permanganate, and three products were obtained; parasulphaminebenzoic acid, anhydroorthosulphaminebenzoic acid, and acid potassiumorthosulphobenzoate; which were the products one would expect to result from the oxidation of a mixture of para- and orthotoluenesulphonamides.

Further evidence that Beckurts' amide, despite the constancy of its melting-point, was a mixture, was given by the following experiment: Equal parts of pure para- and orthotoluenesulphonamides were dissolved in water and the mixture subjected to recrystallization. Two forms of crystals were obtained: long fine needles which melted constantly at 120° and leaves which fused at 108°. Slight impurities lowered the melting-point to 104°–105°, as in the case of Beckurts' amide. F. H. S. Müller,[1] in 1879, mentioned the formation of metatoluenesulphonic acid by the action of sulphurous acid on the corresponding diazo compounds; but beyond the melting-

[1] Ber. d. chem. Ges., **12**, 1348.

points of the amide, anilide and toluidide, gave no details of his work.

Claesson and Wallin,[1] in 1879, claimed that they had obtained metatoluenesulphonic acid by the action of chlorsulphonic acid on toluene. These investigators worked with large quantities of material, bringing together in small portions at a time, 2800 grams of chlorsulphonic acid and 1119 grams of toluene.

The solid parasulphonchloride was removed by cooling the mixture, and the liquid chlorides converted into the amides. Two amides were separated by fractional crystallization, the ortho compound melting at 153°–154°, and the other, supposed to be the meta, melting constantly at 107°–108°. This latter was transformed into the toluenesulphonic acid by being heated with water in a sealed tube to 150°, and various salts were made. These were compared with the salts made by Müller, and also with the analogous salts of the para and ortho acids. From this, despite the fact that they had knowledge of Fahlberg's work, Claesson and Wallin concluded that all three isomeric acids were formed as a result of the action of sulphuric acid on toluene.

The next step in the controversy was taken by R. Otto,[2] who, at the request of Beckurts, examined carefully the specimen of so-called metatoluenesulphonamide, which the latter had obtained three years previously, and which was claimed by Fahlberg to be a mixture, and by Claesson and Wallin, to be metatoluenesulphonamide. The substance, weighing about 10 grams, was heated with hydrochloric acid in a sealed tube. The sulphonic acid formed was converted into the potassium salt, and this was treated with phosphorus pentachloride, with the formation of an oil which soon stiffened and the solid portion of which was freed from the fluid by pressure. This latter portion was dissolved in benzene, from which it crystallized out in large scales which had the same melting-point as paratoluenesulphonchloride, and gave a corresponding amide and anilide. This was conclusive evidence that metatoluenesulphonic acid was not obtained by Beckurts.

[1] Ber. d. chem. Ges., **12**, 1848. [2] Ber. d. chem. Ges., **13**, 1292.

Neville and Winther,[1] in 1880, investigating the formation of amidosulphonic acids by the action of concentrated sulphuric acid, obtained a toluenesulphonic acid by heating orthodiazotoluenesulphonic acid under pressure with alcohol, and by reducing bromotolueneorthosulphonic acid by means of sodium amalgam. By treating the potassium salt with phosphorus pentachloride they obtained a liquid sulphonchloride which gave, in both cases, an amide melting at 106.5°–107.5°, whence they concluded that the acid which they had obtained was metatoluenesulphonic acid.

In 1886 Valin,[2] convinced by the work of Otto, that Fahlberg's views were correct, and that he and Klason had not obtained metatoluenesulphonic acid, again attacked the problem of obtaining the compound. Pechmann's method was followed; an acid was obtained, and a series of salts made and described.

The work of Metcalf,[3] furnished evidence that the decomposition of paradiazometatoluenesulphonic acid by boiling with alcohol under pressure, resulted in the formation of paraethoxymetatoluenesulphonic acid in far greater proportion than metatoluenesulphonic acid. Consequently, neither by Pechmann nor by Valin had the acid been obtained.

Preparation of Metatoluenesulphonic Acid.

In consideration of all this dissentient testimony in regard to metatoluenesulphonic acid and the availability of pure metatoluenesulphonamide in any desired quantity, it was thought desirable to transform the amide into the acid and study its properties. Sealed tubes containing 25 grams of the pure amide and a quantity of hydrochloric acid were heated to 140° for six hours. Upon cooling the tubes contained a mass of clear white fern-shaped crystals, entirely different in form from the amide crystals which had been introduced therein. The tubes were opened and their contents were poured upon a filter and freed from liquid by suction. The crystals were dried and examined. They proved to consist entirely of ammonium chloride.

[1] J. Chem. Soc., **37**, 628. [2] Ber. d. chem, Ges., **19**, 2952.
[3] Am. Chem. J., **15**, 301, and Dissertation.

The fluid portion of the contents of the tube was evaporated down, on a water-bath, water added and reevaporated, and this process repeated until the greater portion of the hydrochloric acid was removed. It was then boiled with potassium hydroxide solution until no further evolution of ammonia was evident. The solution, which contained the potassium salt of metatoluenesulphohic acid and some potassium chloride, was then evaporated down until it solidified in a mass of scales. These were powdered and boiled with alcohol of 95 per cent. The greater portion of the salt dissolved, and separated out on cooling, in a mass of minute scales which nearly filled the beaker. From the mother-liquor more were obtained by evaporation. The undissolved portion was subjected to several more extractions until potassium metatoluenesulphonate no longer crystallized out of the solution. The residue was then examined and found to be potassium chloride. The crystals from the alcoholic solution were collected on a filter and dried. They were then powdered and heated in an air-bath for an hour to 160°. Upon cooling, the substance was rubbed up in a mortar with an equal weight of phosphorus pentachloride. The action was immediate and brisk, and the contents of the mortar became liquid ; but the decomposition was not nearly as violent as when the potassium salt obtained from the diazo decomposition was employed. The liquid chloride mixture was poured into water and thoroughly stirred up. A clear, almost colorless oil gathered on the bottom of the vessel. This was washed several times with water, and then placed in a test-tube in a freezing-mixture. It did not solidify. Müller converted the sulphonchloride, which he obtained, into the corresponding acid by heating it with water in a sealed tube. He stated that it did not decompose with water until it was heated to 130°.

About 5 cc. of the sulphonchloride and 100 cc. of water were placed in a flask connected with an inverted condenser and boiled. Considerable bumping occurred, a small portion of the contents of the flask at times fuming out through the top of the condenser. In about an hour and a half the oily liquid had entirely disappeared. The solution was then

poured into an evaporating dish and boiled until it attained a syrupy consistency. More water was added and it was again evaporated down. This process was repeated until the solution gave no indication of the presence of hydrochloric acid when tested with silver nitrate. All efforts to obtain the metatoluenesulphonic acid in crystalline condition were unsuccessful. After it had become viscous, further heating on a water-bath resulted in giving it a dark, almost black, color. Made clear by boiling with animal charcoal and filtering, it darkened again when kept on the water-bath.

Efforts were then made to crystallize it by evaporation under diminished pressure. About 15 cc. of the syrupy liquid was placed in a round-bottomed flask, which was connected to a filter-pump and kept in boiling water for over an hour. Some water distilled over in the beginning, but ceased coming over after a while. On cooling the contents of the flask remained fluid. The viscous liquid was then placed in a test-tube and kept in a freezing-mixture for half an hour, and though its temperature was lowered to 18° below zero, its condition did not change.

Müller, Pechmann, Pagel, and Klason, all obtained, by evoporating down their acid solutions, a syrup which stiffened to a mass of deliquiscent crystals.

Barium Salt of Metatoluenesulphonic Acid.—A solution of the acid was heated to boiling, and neutralized with barium carbonate. The solution was then filtered and evaporated down to a small bulk. Upon cooling, the barium salt crystallized out in minute scales. With favorable conditions, bunches of apparently rectangular plates about 1/8 of an inch long, were obtained. It is very soluble in water, insoluble in absolute alcohol and ether; soluble in dilute alcohol, and precipitated from its solution in the latter by the addition of a large quantity of ether.

It contains one molecule of water of crystallization.

The salt was analyzed with the following results:

I. 0.2702 gram of the salt gave off, at 180°, 0.0101 gram of water.

II. 0.2208 gram of the salt gave off, at 180°, 0.0080 gram of water.

III. 0.2702 gram of the salt gave 0.1260 gram of barium sulphate.

IV. 0.2208 gram of the salt gave 0.1030 gram of barium sulphate.

	Calculated for $(C_6H_4<^{CH_3}_{SO_3})_2Ba+H_2O$.	Found. I.	II.
H_2O	3.62	3.73	3.62
Ba	27.56	27.42	27.42

The barium salt made by Müller by boiling the free acid with pure barium carbonate gave off two molecules of water of crystallization. Neither from water nor from alcohol could he obtain it in a distinctly crystalline condition.

Lead Salt.—Pure lead carbonate was decomposed by boiling it with a small quantity of the dilute acid. The solution, evaporated down and left to stand, filled up with a mass of crystals consisting of small scales. This salt was very soluble in water, and slightly soluble in strong alcohol. The addition of a large quantity of ether to its dilute alcoholic solution precipitated the lead salt in scales. The analysis of the salt was made with the following results.

For water of crystallization:

I. 0.2480 gram of salt, heated to 160°, gave off 0.0078 gram of water.

II. 0.2394 gram of salt gave off 0.078 gram of water.

III. 0.2212 gram of salt gave off 0.0070 gram of water.

IV. 0.2480 gram of the anhydrous salt gave 0.1278 gram of lead sulphate.

V. 0.3538 gram of the salt gave 0.1813 gram of lead sulphate.

VI. 0.3781 gram of the salt gave 0.1923 gram of lead sulphate.

	Calculated for $(C_6H_4<^{CH_3}_{SO_3})_2Pb+H_2O$.	Found. I.	II.	III.
H_2O	3.17	3.14	3.17	3.16
Pb	36.33	35.21	35.57	34.74

In describing his lead salt, Müller calls attention to the fact that the anhydrous salt absorbed moisture very rapidly, and made it difficult to get good results for the water of crystalli-

zation. No such behavior was noticed in the case of the lead salt here described. The results for water of crystallization agreed as closely as possible with the theoretical, and no difficulty in weighing was experienced. On the other hand, it was found impossible to get good results in the determination of lead. Many analyses were made, the three given above being the best results obtained. Ignition of the salt, alone, or when moistened with sulphuric or nitric acid, invariably caused some reduction. Precipitation in alcoholic solution, as lead sulphate, and filtration throuph a Gooch crucible, gave no better results.

Calcium Salt.—The calcium salt was made by decomposing finely powdered calcite by means of the free acid. It was extremely soluble in water, and could be obtained in crystalline condition only by evaporating the solution almost to dryness, when, upon cooling, it solidified in a mass of scales, which were so matted together that they could not be obtained in a dry condition, by long standing in the air. Upon heating a saturated solution of the calcium salt, a slight milky precipitation occurred, which disappeared on standing, indicating its greater solubility in cold than in hot water. Analyses were made of a specimen which had been dried by standing over sulphuric acid.

I. 0.3989 gram of the calcium salt, heated to 200°, lost 0.0343 gram of water.

II. 0.3196 gram of the calcium salt, heated to 200°, lost 0.0270 gram of water.

III. 0.3989 gram of the salt gave 0.1310 gram of calcium cium sulphate.

IV. 0.3196 gram of the salt gave 0.1051 gram of calcium sulphate.

	Calculated for $(C_6H_4<^{CH_3}_{SO_3})Ca + 2H_2O$.	Found. I.	II.
H_2O	8.61	8.59	8.44
Ca	9.57	9.66	9.67

Müller did not succeed in obtaining the calcium salt of his toluenesulphonic acid in a crystalline condition from its solution in water, and his salts, whether obtained by evaporating the water solution to dryness or by filtration of the boiling

alcoholic solution through a warmed filter, continued to give off water when heated to 200°.

The salt, the analysis of which is given above, was easily obtained in crystalline condition, and gave off all its water of crystallization at 180°–190°; and heated to 200°, it began to darken in color. It was evidently a different compound from that of Müller.

Sodium Salt.—The sodium salt was made by exactly precipitating the barium by means of sodium sulphate from a solution of the barium salt. It is very soluble in water, from which it crystallizes out in large scales when the solution is evaporated down.

Its analysis resulted as follows:

For water.

I. 0.1641 gram of salt lost, upon heating to 150°, 0.0139 gram of water.

II. 0.2060 gram of salt gave off 0.0175 gram of water.

For sodium.

III. 0.1502 gram of the salt gave 0.0549 gram of sodium sulphate.

IV. 0.1885 gram of the salt gave 0.0683 gram of sodium sulphate.

	Calculated for $\left(C_6H_4<\frac{CH_3}{SO_3}\right)Na+H_2O$.	Found. I.	II.
H_2O	8.49	8.47	8.49
Na	10.85	10.91	10.73

The sodium salt obtained by Müller did not crystallize well from water, and contained but one-half a molecule of water of crystallization.

Potassium Salt.—The potassium salt was made, as was the sodium, by the exact precipitation of a solution of the barium salt. This salt crystallized in thin scales and was easily soluble in water, sparingly so in strong alcohol. It dissolved to a great extent in hot, ordinary alcohol, from which it separated out in small scales. Addition of ether to the alcoholic mother-liquor caused a copious precipitation.

The following are the results of its analysis:

I. 0.2146 gram of the salt, heated to 180°, gave off 0.0096 gram of water.

II. 0.1980 gram of the salt gave off 0.0089 gram of water.

III. 0.2146 gram of the salt gave 0.0844 gram of potassium sulphate.

IV. 0.1980 gram of the salt gave 0.0773 gram of potassium sulphate.

	Calculated for $(C_6H_4<^{CH_3}_{SO_3})K+\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	4.11	4.47	4.49
K	17.75	17.63	17.50

This potassium salt agrees with that of Müller in solubility and water of crystallization.

Silver Salt.—Pure silver carbonate, obtained by precipitating a solution of silver nitrate by means of sodium carbonate, was decomposed in a boiling solution of the acid. Upon filtering and evaporating down to a small volume, bunches of rectangular plates were obtained, which showed a micaceous cleavage on breaking apart. These were easily soluble in water, and to a much lesser extent in alcohol. From their solution in the latter they were precipitated by the addition of ether. They contained no water of crystallization, and blackened on being exposed to the light.

Analyzed :

I. 0.2061 gram of the salt gave 0.0080 gram of silver.

II. 0.2640 gram of the salt gave 0.1023 gram of silver.

	Calculated for $C_6H_4<^{CH_3}_{SO_3Ag}$.	Found. I.	II.
Ag	38.71	38.81	38.75

Magnesium Salt.—The magnesium salt was made by boiling pure magnesium carbonate in a solution of the acid. After neutralizing the acid the solution was filtered and reduced in volume by evaporation. On standing the salt crystallized out in beautiful long transparent thick prisms, which lost water rapidly in the air. Their crystalline structure appeared to be orthorhombic and hemihedral. The magnesium salt is slightly soluble in alcohol, from which it is precipitated by ether in minute plates. The property of rapidly losing water of crystallization, when exposed to the air, was not noticed in any of the other salts of metatoluenesulphonic acid. But the magnesium salt, which consisted of beautiful large, transparent crystals, some of them an inch and over in length

when first removed from the mother-liquor, became opaque after a brief exposure to the air, and disintegrated upon long standing.

Subjected to analysis it yielded the following results:

For water of crystallization.

I. 0.2050 gram of the salt lost, when heated to 150°, 0.0644 gram of water.

II. 0.2166 gram of the salt gave off, at the same temperature, 0.0691 gram of water.

	Calculated for $(C_6H_4{<}^{CH_3}_{SO_3})_2Mg+10H_2O$.	Found. I.	Found. II.
H_2O	32.05	31.45	31.90

For magnesium:

I. 0.2636 gram of the anhydrous salt gave 0.0865 gram of magnesium sulphate.

II. 0.2797 gram of the anhydrous salt gave 0.0896 gram of magnesium sulphate.

	Calculated for $(C_6H_4{<}^{CH_3}_{SO_3})_2Mg$.	Found. I.	Found. II.
Mg	6.56	6.55	6.40

Manganese Salt.—A solution of the barium salt was treated to exact precipitation with manganous sulphate. Upon reducing the solution to a small bulk and cooling, the manganese salt crystallized out in long prisms, which were easily soluble in water, and to a slight extent in alcohol. From the alcoholic solution they were precipitated in the form of bunches of small needles.

The following are the results of the analysis:

I. 0.2150 gram of the salt gave off, when heated to 200°, 0.0461 gram of water.

II. 0.2708 gram of the salt gave off 0.0588 gram of water.

III. 0.2150 gram of the anhydrous salt gave 0.0326 gram of manganous manganic oxide.

IV. 0.1689 gram of the salt gave 0.0326 gram of manganous manganic oxide.

	Calculated for $(C_6H_4{<}^{CH_3}_{SO_3})_2Mn+6H_2O$.	Found. I.	Found. II.
H_2O	21.44	21.44	21.67
Mn	10.89	10.92	10.93

Zinc Salt.—The zinc salt was made by treating a boiling solution of the acid with pure zinc carbonate. After filtering and evaporating down the solution, long slender prisms were deposited. They were soluble in water and alcohol, and were precipitated from the alcoholic solution in minute scales upon the addition of ether. The salt was very stable, and the crystals retained their lustre after long exposure to the air. It was analyzed for zinc, by precipitating it as carbonate and igniting the latter.

I. 0.3377 gram of the salt lost upon being heated to 180°, 0.0695 gram of water.

II. 0.3106 gram of the salt lost upon being heated to 180°, 0.0638 gram of water.

III. 0.3377 gram of the salt gave 0.0527 gram of zinc oxide.

IV. 0.3106 gram of the salt gave 0.0482 gram of zinc oxide.

	Calculated for $(C_6H_4{<}^{CH_3}_{SO_3})_2Zn+6H_2O$.	Found. I.	Found. II.
H_2O	20.97	20.58	20.54
Zn	12.62	12.51	12.52

Copper Salt.—The copper salt was obtained by precipitating barium sulphate from a solution of the barium salt by means of copper sulphate. Upon evaporating the solution nearly to dryness and cooling, a mass of light blue scales was obtained. The copper salt was very soluble in water and ordinary alcohol, very slightly soluble in absolute alcohol, and insoluble in ether. The addition of ether to an alcoholic solution of the salt, caused its precipitation in minute, almost white, scales. No very satisfactory determination of water of crystallization of the copper salt could be obtained.

On heating 0.2995 gram of the salt to constant weight in an air-bath at 170°, it was found to have lost 0.0450 gram of water, or 15.02 per cent. The theoretical percentage of water, assuming the salt to contain four molecules of water of crystallization, is 15.03. The determination of the water of crystallization of different specimens obtained by precipitating the salt from its alcoholic solution by means of ether, gave no concordant results.

The copper was determined in the anhydrous salt by electrolysis.

I. 0.2545 gram of the anhydrous salt gave 0.0401 gram of copper.

II. 0.3725 gram of the salt gave 0.0585 gram of copper.

Calculated for $(C_6H_4 <^{CH_3}_{SO_3})_2 Cu$.	Found. I.	II.
15.55	15.70	15.70

Metatoluenesulphonanilide. — This substance was made by bringing together some metatoluenesulphonchloride and a slight excess of aniline. The action was extremely rapid. The flask became very hot and its contents solidified in a crystalline mass. The contents of the flask were then boiled with dilute hydrochloric acid, in order to remove any unacted upon aniline, and the anilide was then crystallized from ether, in which it was very soluble. A yield of small prismatic crystals was obtained. The anilide was insoluble in cold water and dissolved only to a very slight extent in boiling water. It was extremely soluble in alcohol, from which it crystallized out in large monoclinic prisms. It melted sharply at 96°.

Müller and Wiesinger[1] mention a metatoluenesulphonanilide, which melted at 72°. They obtained the meta acid by treating the diazo compound with sulphurous acid.

Metatoluenesulphontoluide.—The ortho- and paratoluides of metatoluenesulphonic acid were made by bringing together metatoluenesulphonchloride and the proper toluidine, the latter in slight excess. The reaction was very rapid and violent, part of the contents of the flask volatilizing. The excess of toluidine was removed by warming the mixture with dilute hydrochloric acid, and washing several times with water. Both toluides are well-crystallized compounds, insoluble in water, but very soluble in ether, alcohol and benzene.

The metatoluenesulphonorthotoluide crystallized in prisms and thick plates, and melted at 108°.

The metatoluenesulphonparatoluide crystallized in small prisms and melted at 106°. The toluide mentioned by Müller and Wiesinger,[2] melted at 103°.

Conclusion.

From the experiments detailed in the first part of this work, we may conclude that:

1. When paradiazometatoluenesulphonic acid is decomposed

[1] Ber. d. chem. Ges., **12**, 1348.

[2] Ber. d. chem. Ges., **12**, 1348.

in alcohol in the presence of an excess of some alkalies and zinc dust, only the hydrogen reaction takes place.

2. When the decomposition takes place in alcohol saturated with ammonia, the ammonium salt of paratoluidinemetasulphonic acid is formed.

3. The nature of the alcohol, as regards methyl and ethyl alcohol, has no influence on the reaction.

4. If we except the case of decomposition in the presence of calcium carbonate, countenance is given to the suggestion that the neutralization of free acid by the presence of some substance which can combine with it, determines the hydrogen reaction.

But why calcium carbonate does not effect this purpose, which, on the other hand, is easily accomplished by zinc dust, has yet to be determined.

From the study of metatoluenesulphonic acid and its salts, we may conclude that the compounds obtained by Müller and others who employed analogous methods for obtaining them, were impure products.

This follows especially from a comparison of the properties of the amide, and from the fact that the sulphonchloride suffers decomposition into the acid when boiled with water in an open vessel, while the sulphonchloride of Müller did not decompose until heated to 130° in a sealed tube.

No detailed comparison of the salts of metatoluenesulphonic acid herein described, with those made by other methods than those of Müller was made, for previous work in this laboratory, by Fahlberg and Metcalf showed conclusively that they were not true meta compounds.

The analyses were calculated on the basis of the following atomic weights:

H	1	Na	23
O	16	K	39
C	12	Ca	40
N	14	Ba	137
Ag	108	Cu	63
Mg	24	Mn	55
Zn	65	Pb	207
S	32		

JOHNS HOPKINS UNIVERSITY,
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Biographical.

John Joseph Griffin was born near Corning, N. Y., June 24, 1859. His early education was obtained in the public schools of Lawrence, Mass., graduating from which he entered Ottawa College (Canada) in 1878. He received the degree of Bachelor of Arts from this institution in 1881, and two years later that of Master of Arts, and in the same year entered the Ottawa Diocesan Seminary. Ordained priest, May 1, 1885, he spent a year as instructor in elementary physics in Ottawa College, after which he undertook the work of the ministry in the archdiocese of Boston. In September, 1887, he returned to Ottawa College as instructor in elementary physics and chemistry, which position he held for three years. In 1890 he entered Johns Hopkins University as a graduate student in chemistry, with physics and mathematics as subordinate subjects. While pursuing his studies at Johns Hopkins University, he conducted classes in chemistry at St. Joseph's Seminary, and Notre Dame of Maryland.